APPLICATIONS OF GROUP THEORY TO THE
VIBRATIONS OF METHANE MOLECULES IN THE GASEOUS AND SOLID PHASES


## by <br> CONSTANTINE PAPANASTASOPOULOS, B.Sc.

## A Thesis

Submitted to the Physics Department

$$
\begin{gathered}
\text { in Partial Fulfilment of the Requirements } \\
\text { for the Degree of } \\
\text { Master of Science }
\end{gathered}
$$

MCMASTER UNTVERSITY
Hamilton, Ontario

TITLE: Applications of group theory to the vibrations of methane molecules in the gaseous and solid phases.
AUTHOR: Constantine Papanastasopoulos, B.Sc.
(Université de Montreal)
SUPERVISOR:
NUMBER OF PAGES: VI, 46
SCOPE AND CONTENTS:
We present a discussion of the application of group theory to the particular case of solid methone,in all its crystalline phases. We also employ the quantum mechanical mean approximation to derive the mean square angle of deviation 0 the methane free molecule. By means of group theory we derive the nomal modes, the symmetry coox dinates and the auclear spin functions of methane, which may be found useful for many other purposes in the study of methane. Finally, using these results, we give a discussion of the infrared and Ramen spectra, based on group theory again, to explain the observed transitions of the methane molecule in its condensed phases. We conclude that the ${ }^{\prime}$ mppe transitions are caused by changes in molecular orientation Phase I is probably disordered, while phase II has structure of symmetry $D_{2 d}$ Pbase III (of $\mathrm{CD}_{4}$ ) is ordered but of lower symatry and unclear structure.

A possible explanation probably requires an arrangement have ing more molecules per unit cell thas in phases I and II.

## ACKIVOWLEDGEMENTS

I wish to gratefully express my sincere appreciation to Professor D.A.Goodings smy thesis supervisor, for his patient guidance, encou ragement, valuable suggestions and discussions during the course of this work.

I an in debt to the Physics Department of McMaster University and the Government of Ontario for financial suport under the form of a teaching assistantship or graduate fellowship.

TABLE OF CONTENTS
Page ..... I
Chapicer i normal modes of vibration or the free molecule ..... 4
Introduction ..... 4
The normal modes of vibration ..... 5
Application to methane ..... 8
Syminetry coordinates ..... I6
Symaetry coordinates of the methane molecule ..... I8
CHAPTER II MOLECULAR FIELD APRROXIMATION RETHOD ..... 25
Introduction ..... 25
Description of the system ..... 26
Construction of the density matrix ..... 26
Mean field potential ..... 28
Energy calculation ..... 28
Thermodynamics ..... 29
Entropy,Free energy ..... 3 I
Mean deviation angle ..... 32
Application to methane (free molecule) ..... 32
CHAFTER III NUCLEAR SPIN WAVE FUNCTIONS FOR METHANE ..... 36
Chapser iv INFRARED and raikiv specera and Stuctures of Crystallitie phases of methane ..... 4 I
Introduction ..... $4 I$
Spectra from crystalline phases of methame ..... 42
Refereinces ..... 46

## LIST OF FIGURES

|  |  | Page |
| :---: | :---: | :---: |
| FIG.I | The Hethane molecule | 9 |
| FIG. 2 | The breathing mode ( $A_{I}$ ) of the methane molecule | I4 |
| FIG. 3 | The three dimensional normal modes of the methane molecule ( $x, y, z$ ) | I5 |
| FIG. 4 | The three dimensional normal modes of the methane molecule( $x y, y z, z x$ ) | I5 |
| FIG. 5 | The two dimensional nomal modes of the rethane molecule | I4 |
| FIG. 6 | The Internal coordinates of the methane molecule | I9 |
| FIG. 7 | Diatomic molecule at equilibrium and rotated wrt. SFA for the determination of its orientation | 35 |
| FIG. 8 | Methane molecule at equilibrium Wris.SFA, and rotated to indicate the IDA | 35 |

## IIST OF TABLES

|  | İ | Page |
| :---: | :---: | :---: |
| T.I.I | Character table of the $\mathrm{T}_{\mathrm{d}}$ symmetry group | IO |
| T.I. 2 | Character table of the $\Gamma_{I 5 \times I 5}$ representation | IO |
| T.I. 3 | Character table of the rotational and vibrational representations | I2 |
| T.I. 4 | Character table of the $I_{r}$ and $I_{\theta}$ repre sentations for the symmetry coordinates | 20 |
| $\begin{array}{r} \text { T.I. } \\ \begin{array}{r} 5 \\ 5 \mathrm{a} \\ 50 \end{array} \end{array}$ | Table indicating how the difserent internal coordinates of the methane molecule transform, under the operations of the $\mathrm{T}_{\mathrm{d}}$ group | 20 |
| T.I. 6 | $\gg$ | 22 |
| T.I. 7 | Table of the Symetry coordinates for the methane molecule | 24 |
| T.III.I | Table containing the Vibro-nuclear spin wave functions for the methane molecule | 40 |

## IMTRODUCTION

In I929 Clusius ${ }^{(1)}$ noted the existence of a $\lambda^{\text {-type }}$ singularity in the spe cific heat of the solid $\mathrm{CH}_{4}$ at $20.4^{\circ} \mathrm{K}$. In 1939 an X -ray study carried out by A.Schallarach ${ }^{(2)}$ revealed a f.c.c structure of the molecular lattice both above and below $20.4^{\circ} \mathrm{K}$. This result was also confirmed and extended to all phases of $\mathrm{CD}_{4}$ in a recent measurement by Greer and Meyer ${ }^{(3)}$ who working with more recent instruments did not notice the parasitic lines which had been observed by Shallamach in the powder pattern of $\mathrm{CH}_{4}$.

The different theoretical and experimental studies on methane whio ch will be reffered to belowshave led to the important and final conclu sion, that the observed phase transitions correspond to changes in the orientational structure of solid methane. As the methane sructure could not be fully understood from experimental studies only,theoretical predictions have helped provide a basis for the discussion of the experimental results . Among these the molecular field approximation used by James and Keenan ${ }^{(4)}$ which is fully developed in this work(Ch. II) has proven the most succesinul. They discussed the three solid phases of $\mathrm{CD}_{4}$, treatm Ing the crystal as an focec array of spherical rotators, where molecular and latice vibrations were neglected. In the interaction potential only octopole-octopole terms between nearest neighbours are retained. lower multipoles, disappearing by symetry in an undistorted methene tetrahedo ron.

On the other hand Nagamiya ${ }^{(5)}$ studied how the energy levels of the free rotator are split by the crystal field due to the neighbouring molecules. Only little additional insight concerning the arrangement of the me thane tetrahedra can be gained from IRabsorption and Raman scattering, due to the lack of one to one correspondence between observed Iines and the symmetry of the unit cell. In adition, it seems questionable whether the instrumental resolution available in these measurements was sufficient. In any case we discuss here the experimental results of Anderson and Savoie ${ }^{(6)}$ on the basis of group theory and we cone to the same conclusion as the others by different procedures, concerning the structure of the phases of solid methane.

Recently another method was employed by W.Press ${ }^{(7)}$ for a better understanding of the orientational structure of methane, that of neutron difIraction. Here again, as all methods have shovm,it was found that Phase I is disordered. The structure of phase II was found to agree with that pro edjeted by James and Keenan. ${ }^{(4)}$ It was also found that Phase III seems to arise by small distortions of the orientational structure in phase II.

In general, in discussions of the structures of the three solid phases of $\mathrm{CH}_{4}$ and $\mathrm{CD}_{4}$, everyone agrees, that the carbon atons occupy f.c.c lattice sites in phases $I$ and II, and that this picture may be taken as a good approximation for phase III.

In our discussion we add the possibility of a probable rearangement of the unit cell in phase III to one having more molecules, as indicated by the experimental results of the infrared spectra of Anderson and Savole ${ }^{(6)}$

Thus the phase changes may readiny be understood as trensitions
in the oxientational oxder of the methane tetrahedra.
The above conclusion constitutes the most valid explanation.

## CHAPTER I

NORMAL MODES OF VIBRATION OF THE FREE MOLECULE

## INPRODUCTIOR

The determination of the normal modes of a system and their frequency of vibration is very often a tedious process. Group theory can be used to en able some simplification.

The definition of normal coordinates means that the Lagrangian of the system can be expressed in terms of squares of the normal coordinates and their derivatives only.

So the K.E and the P.E are writen in tems of nomol coordinates.

$$
\begin{array}{ll}
T=\frac{I}{2} \sum_{i=1}^{3 N} \dot{Q}_{i}^{2} & \text { (I) } \\
V=\frac{I}{2} \sum_{i=1}^{3 N}\left(\omega_{\dot{j}} Q_{\dot{j}}\right)^{2} & \text { ( } 2 \text { ) } \tag{2}
\end{array}
$$

where $Q_{i}$ are the normal coordinates, forming a coordinate basis where $T$ and $V$ are diagonal in this particular representation.

In case of molecules, $N$ is the no of atons ( $N$-atomic molecule), $3 N$ is the no. of degrees of freedom, $j$ labels the $j$ th atom executing small oscillations around equilibrium and $Q_{j}$ is the displacement from equilibrium.

Introducing canonical momentura

$$
\begin{equation*}
p_{j}=\frac{\partial T}{\partial \dot{Q}_{i}} \tag{I.3}
\end{equation*}
$$

equs ( $I_{0} I$ ) and ( $I_{2}$ ) can be used to construct the Quantum mechanical Hamiltomian, which is writen in terms of normal coordinates

$$
H=\frac{T}{\sum} \sum_{j=1}^{3 N}\left(p_{j}^{2}+\omega_{j}^{2} Q_{j}^{2}\right)
$$

and using $f_{j}=-\frac{\partial H}{\partial Q_{j}}$
we get eqns of notion :

$$
e_{j}+\omega_{j}^{2} Q_{j}=0 \quad\left(I_{0}\right)
$$

having solution

$$
\left.Q_{j}=Q_{j}^{0} \cos \left(\omega_{j} t+\varphi\right) \quad \text { (I. } V^{2}\right)
$$

where $\omega_{j}=2 \pi v_{j}$ is the frequency of the $j^{\text {th }}$ normal mode.
If we now take a molecule and periorm a symmetry operation on it. then the physical state of the molecule is unaffected by this operation so that $T, W$ and $I$ are invariant under transformation of the coordinates corresponding to this operation.

The normal modes of vibration :
We shall set up now, the general method which can be used for any molecule which belongs to a symetry group and then this general nethod will be applied in the case of the Tetrahedral ( $T_{d}$ ) symetry group which methane $\left(\mathrm{CH}_{4}\right)$ belongs to o

Let us consider a system (molecule) consisting of Nif particles (atoms)at their sites. If energy is imparted to the molecule (sheken). then each atom will execute a complex vibratory motion around its equili brium positionsin such a way that the motion of all the atoms is in phase.

A basic requirement is, of course, that the net resuit of this motion is such that, there is no translation or rotation of the nolecule (Maturally, if it happens all the moleculcs at the same instant of time to nove in the same direction, the molecule will translate along this directions so these modes will be translational.)

There are , of course, three translational and three rotational modes. For linear nolecules therearponly twe rotational degrees of freedomse cause rotations can only take place around two axes, So for polyatomic molecules or ions renain $3 \mathrm{~N}-6$ vibr degrees of ireedom and for in near molecules or ions $3 \pi-5$ vibr.degrees of freedom.

## STEPS

a.) Establish a set of Cartesian vectors $X_{i}, y_{i}, z_{i}$ on each atom $i$ at its equilibriun position, representing the displacement of the atom from equilibrium
b.) Determine the dimension of conifguration space $3 \mathbb{N}$, where is the no. of atoms of the molecule and deduce the vibratory degrees of free dom.
c.) Deduce the"symmetry group" of the equil. positions(i.e to accorroda te the molecule to one of the known symmetry groups). Write down the character table of the group.
d.) Deduce from geometrical considerations the characters $\mathcal{X}(R)$ of the 3N X 3 N representation $\mathrm{I}_{3 \mathrm{NX} 3 \mathrm{~N}}$. To calculate the characters of $\mathrm{I}_{3 \mathrm{NX} 3 \mathrm{~N}}$ consider the ffo
i.) Oaly those nuclei contribute to the characters, which transform into themselves; that is in the $3 \mathbb{N} X 3 \mathbb{N}$ "supermatrix" that corresponds to $I_{3 N K}$ SN representation for the whole molecule, observe that only those atoms contribute to the character ofthe particular operation $R$, which do not nove when the system is subjected to this certain operation $R_{0}$ In the $3 N X 3$ R supermatrix represeating $R$, all the $3 \times 3$ submatrices cor responding to the parificles whicin change nosicion are displaced froil the diagonal (so they do not contribute to the character), on the other hand for each undisplaced particle there is a $3 \times 3$ matrix whose diagon
-21 coincides with the diagonal of the $3 N X$ 3N supermatrix. ii.) A $C_{n}^{k}$ operation (rotation) contributes for each undisplaced atomm $I+2 \cos \frac{2 n k}{n}$ to the character of the supermatrix

$$
\begin{equation*}
x\left(c_{n}^{k}=I+2 \cos \frac{2 n k}{n}\right. \tag{0}
\end{equation*}
$$

where $k$, is the no.of units of rotation.
A $S_{a}^{k}$ improper rotation, contributes for each undisplaced atom;

$$
\begin{equation*}
x\left(s_{n}^{k}\right)=-I+2 \cos \frac{2 \pi k}{n} \tag{.}
\end{equation*}
$$

A $\sigma$ operation(reflection on a plane), $\mathcal{X}(\sigma)=+I$, and Identity al ways $X(E)=3 E \cdot(1,8)_{a}$
e.) From the characters $X(R)$ of the $I_{3 N X} 3 N$ representation, subtract the characters $X_{T}(R)$ belonging to translations and $X_{R}(R)$ belonging to rotations, which are known since translations transform like $x, y, z$, and rota tions like $R_{z s} R_{y} R_{z}$ and exist in the character tables of the group. So the characters of the representation corresponding to vibrato ry degrees of freedom is;

$$
\begin{equation*}
X_{V}(R)=\chi(R)-X_{T}(R)-X_{R}(R) \tag{I.9}
\end{equation*}
$$

f.) Decompose the $I_{3 N X 3 N}$ acc. to formula:

$$
\begin{equation*}
I_{3 N X 3 N}=\sum_{i=1}^{K} c_{i} I_{i} \tag{I.IO}
\end{equation*}
$$

where $I_{i}$ are representations of the $T_{d}$ group and:

$$
\begin{equation*}
c_{i}=\frac{S}{H}\left[\sum_{k} \pi_{k} X_{i}(R) K(R)\right] \tag{I.II}
\end{equation*}
$$

where $C_{i,}$, apecifies the independent normal modes.

## Application to methane :

Following the previously reffered steps, we deftne and decompose mo tion along three Cartesian axes $x_{i}, y_{i}, z_{i}$, situated at the equilibrium position of every atom. (fig. I). Methane has $\mathbb{N}=5$ atoms, Hydroegen $H$ (A) $\mathrm{H}(\mathrm{b}), \mathrm{H}(\mathrm{c}), \mathrm{H}(\mathrm{d})$ and Carbon (c), so $3 \mathrm{~N}=$ I5 degrees of freedom and $3 \mathrm{~N}-6=9 \mathrm{vi}$ bradegrees of Exeedom.

The point group of $\mathrm{CH}_{4}$ is the full tetrahedral $\mathrm{I}_{\mathrm{d}}$ having character table(T.I.I). We deduce the characters of the $I_{3 N X} 3$ representation (of the $I_{I 5 X I 5}$ supermatrix), the characters will be $X(E)=I 5, X\left(C_{2}\right)=I+2 \cos \frac{2 \text { it }}{2}$
 move about $x, y, z$, except the Carbon at the origin of xyz;so oniy the carm bon contributes in the character(the rest are off diagonal).

So $X\left(C_{2}\right)=-I$.
Similarly $X\left(C_{3}\right)=0$ for every unnoved atom, so $X\left(C_{3}\right)=0$ for the super matrix.
$\chi(\sigma)=$ I for each unnoved atom, every diagonal plane contains $2 H$ at oms plus the carbongioe three atoms which naturally are unchanged as being on the plane, so for any one of the reflection planes there are three unnom ved atoms and so three non zero diagonal elements in the supermatrix, there fore $X\left(\sigma^{\circ}\right)=3$.
$\chi\left(S_{4}\right)=-I$ since only the carbon atom remains unnoved in this opera tion.

We tabulate the characters of the $I_{5 X I 5}$ representation in table (I.I.2)


The methane molecule with the Cartesian axes at the site of each of the five atons, indicating the three components of the displacement from equilibrium.


Translations transform like $x_{g} y_{g} z_{g}$ and from ( $\left.\mathbb{A}_{0} I_{G} I\right)_{8}$ we see that they transform ace to $\mathbb{T}_{2}$ :

So $X_{T}^{r}(R) \quad 3 \quad 0 \quad-I \quad I \quad-I$
 they transform acceto $\mathrm{T}_{\mathrm{I}}$

We then tabulate these in (T.I.3) where $X=X_{15 X 5}-\left(X_{T}+X_{R}\right)$
Representation ITSXI5 is decomposed acc. to the formiae(I.IO). (I .II):

Here

$$
\begin{aligned}
C_{A_{I}} & =\frac{I}{2}\left[I_{0} I_{\sigma} I 5+8 . I_{0} 0+3 . I \cdot(I)+6 . I .3+6 . I(G I)\right] \\
& \approx I
\end{aligned}
$$

and similarly:

$$
\mathrm{C}_{\mathrm{A}_{2}}=\mathrm{O}_{\theta} \mathrm{C}_{\mathrm{D}} \approx \mathrm{C}_{\mathrm{I}_{\mathrm{I}}}=\mathrm{I}_{9} \mathrm{C}_{\mathrm{T}_{2}=3}=3
$$

So TI5XI5 is decomposed as:

$$
I_{I 5 X I 5} \propto A_{I}+E+T_{I}+3 I_{2}
$$

and since $I_{T} I_{R^{s}}$ are $I_{2}$ s $I_{I}$ respectively we have finally:

$$
I_{V=} I_{I 5 X I 5}=\left(I_{T}+I_{R}\right)=A_{I}+E+2 T_{2}
$$

These representations correspond to mine normal modes of the bethe ne molecule. Any vibrating system that possesses a set of symmetry opes ations, the normal modes of that system "belong to ${ }^{\text {n }}$ or transom accord ing to ${ }^{10}$ one of the inrederapreseatations of the group of those symmetry operations.

If the dimension of the representation $i s$ greater than unitysthis

|  | E | $8 C_{2}$ | $3 C_{2}$ | $6 \sigma_{d}$ | $6 S_{4}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $I_{\text {I5 }} \times 15$ | I5 | 0 | -I | 3 | -I | $A_{I}+E+T_{I}+3 T_{2}$ |
| $I_{T}$ | 3 | 0 | -I | I | -I | $T_{2}$ |
| $I_{R}$ | 3 | 0 | -I | -I | $I$ | $\mathrm{T}_{\mathrm{I}}$ |
| $I_{T}+I_{R}$ | 6 | 0 | -2 | 0 | 0 | $\mathrm{T}_{\mathrm{I}}+\mathrm{T}_{2}$ |
| $I_{V}$ | 9 | 0 | $I$ | 3 | -I | $A_{1}+E+2 T_{2}$ |

means that there is a set of normal modes, equal in number to the dimen sion of the representation, all of which have the same frequency of vibra tion. They are said to constitute a set of "degenerate nomal modes".

The individual normal modes can be thought of as the components of a vector which forms a basis of this irred representation, that is the degeneracy of the normal modes equals the dimension of the irred.re presentation to which it belongs.

In methane, we have ; one non degenerate, one two-fold degenerate and two three-fold degenerate normal mode frequencies.

We draw these normal nodes:
$A_{I}$ mode simplest : called "totally symmetrical" or "breathing mode"
(fig. 3 ). In this all the $H$ atoms have displacements along the directions of the C-H bonds,being equal in magnitude and all directed outwards from the C atom, which itself remains at rest.

Threefold $T_{2}$ : To determine the nature of the threefold degen.nomal modes, we use the fact that these normal modes form a basis of the degene rate representation $\mathrm{T}_{2}$ of the point group of the molecule. There are two sets of functions which transform acc. to $T_{2}:$ the ( $x, y, z$ ) and the ( $x y$, $\mathrm{yz}, \mathrm{zX})$; so the directions of normal modes will be along $\mathrm{x}, \mathrm{y}, \mathrm{z}_{\mathrm{y}}$ in the one set(fig. 4 ), and on the planes(along the diagonals) in the other sete (fig.5). The fact, that we must no have translational motion, allows us to consider the motion of the carbon atom in opposite direction of the motion of the 1 l atoms.

Twofold $E:\left(f_{i g} 6\right)$ shows how the 2-dimonormal modes move.
$A_{\text {I }} M O D E$ TOTALLY SYIMETRICAL OR BREATHTMG MODE OF THE METMATE MOLECULE


E (Twofold) MORMAL MODES OE WHE BETHANT MOLECULE


y

fig. 4


I. 5

Symmetry coordinates :
Displacement pattern of atons can be ropresented in terms of internal coordinates" (such as spacing between atoms,angles between bond directions) or in terms of"external coordinates" (such as Cartesian or Polar).

Introduce "Symetry coordinates" as linear combination of the inter nal coordinates, which transform irreducibly according to the representations of the symmetry group of the molecule.

$$
\begin{equation*}
S\left(I_{g}\right)=N \sum_{R} X_{g}(R) R S_{I}^{(\mathcal{B})} \tag{I.I2}
\end{equation*}
$$

where according to the definition $S\left(I_{G}\right)$ is symmetry ccordinate transforming acc.to irreducible representation $I_{G^{\prime}}$ expressed as linear cormbination of the internal coordinates $R S_{I}$, where $S_{I}$ is any internal coordinate, $R$ is any symmetry operation of the group, ${ }^{R S}$ I is the internal coordinate that resulte from applying operation $R$ to $S_{I}$, and $N$ is some normalization factor. Remark: As we see $R S_{I}$ consists of a set of all possible values that an intemal coordinate can take,for these values a table will be constructed. The internal coordinates in general, may differ frora the normal co ordinates of the molecule.

In molecules in general we take as internal coordinates,interato mic distances and angles between the atomic bonds,so in our procedure, we use our internal coordinates as a basis for two representations $I_{g}$; the $I_{r}$ or $I(r)$ of distances betreen the atoms and $I_{\theta}$ or $I(\theta)$ of the angles between the different $r_{i}$ and $x_{j}$ 's and form the character table, applying the operations of the group and simply counting the number of unchanged coordinates. In constructing the character tablegwe have always $X^{i}(\mathbb{F})$ equ al to the no. of symetry coordinates of type i (e.g: $\mathbb{K}^{3}(E)$ character of symmetry coordinate of type $r$ ).

Another fact which arises here, as we shall see is that anozg the number of irreducible representations we get such ones which do not appear when we calculate the normal modes as we did before.

Because of this ge get no. of internal coordinates more than the number of degrees of freedom (in the case of methane we obtain Io intecoor dinates $6 \theta_{i j}$ and $4 x_{i}$ shat is one nore than the 9 degro of freedom)

This will cause a "redundancy" which is expressoc in the presence
of the same representation $\left(A_{y}\right.$ in $\left.C H_{4}\right)$ in both $T_{r} I_{B^{\circ}}$
Finally the redundant representetion will be excluded.

Symmetry coordiates of the methane molecule:
We choose the internal coordinates to be the distances $r_{j}$ between the atoms $C$ and the $H(i)$ and the angles $G_{j}$ between the $r_{i}$ and $r_{j}{ }^{\prime} s_{0}$

In fig. 6 are shown $r_{i}=r_{I}, r_{2}, r_{3}{ }^{2} r_{4}$ and $\theta_{i j}=\theta_{I 2}, \theta_{I 3}, \theta_{I 4}, \theta_{23}, \theta_{24} ; \theta_{34}$ so $X^{r}(E)=4$ and $X^{\theta}(E)=6 \theta_{i j}$, is unchanged when $x_{i}$, and $r_{j}$ are interchan ged, so we do not count distinctly $\theta_{i, j}$ and $\theta_{j i}$ ).

We form now the character table (T.I.4) for the two representations $I(x)$ and $I(\theta)$; as an illustration we give the derivation of the charac ter for the operation $C_{3}$. Rotating about $C_{3}$ axis, that is along some $r_{i}$ the only one $r_{j}$ which does not change is the one around which we rotate so $X^{r}\left(C_{3}\right)=I$

We decompose now the representations $I_{r}$ and $I_{0}$ into the representations of the $T_{d}$ group using (I.IO), (I.II); so $C_{A_{I}}=C_{T_{2}}=I$ and $C_{E}=C_{A_{2}}=$ $=C_{m_{1}}=0$, therefore (I.IO) gives:

$$
\begin{equation*}
I_{r}=I(r)=A_{I}+T_{2} \tag{I.I3}
\end{equation*}
$$

for $I$ (0) representation $C_{A_{I}} \Rightarrow C_{E} \Rightarrow C_{T_{2}}=I$ and $C_{A_{2}}=C_{T_{I}}=0$; so

$$
\begin{equation*}
I_{\theta}=\Gamma(\theta)=A_{I}+E+T_{2} \tag{I.I4}
\end{equation*}
$$

We see immediately that $A_{I}$ exists in both (I.I3) and (I.I4) so it is redundant.We dexive the symetry coordinates now by taking the inear combination of the iaternal coordinates $r_{i}{ }^{\prime s}$ and $\theta_{i j}{ }^{\prime} s_{0}$

Choose $S_{I}=r_{I}$ internal coordinate; the following table (T.I.5) shows how $r_{I}$ transforms under the different operations of the group ; in this Specific case $x^{\prime}$ goes to itself under $\mathbb{E}_{\text {, }}$ it goes twice into itself under

fig. 6 - The intemal coordinates $x_{i}=r_{I}, r_{2}, r_{3}, r_{4}$ and $\theta_{i j}=\theta_{I 2}$, $\theta_{\text {I3 }}, \theta_{\text {I4 }}, \theta_{23}, \theta_{24}, \theta_{34}$ of the methane molecule.

| T ${ }_{2}$ |  | E | $\mathrm{C}_{3}$ | ${ }_{2}$ | $\mathrm{S}_{4}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{array}{ll} I_{r} & I(r) \\ I_{\theta} & I(\theta) \end{array}$ |  |  |  |  | 0 |  | $\mathrm{A}_{\mathrm{I}}+\mathrm{T}_{2}$ |
|  |  | 6 | 0 | 2 | 0 | 2 | $\mathrm{A}_{1}+\mathbb{E}+\mathrm{T}_{2}$ |
| $\mathrm{Pr}_{\mathrm{I}}$ |  |  | T.I. 5 |  |  |  |  |
| R | r | $r_{2}$ | $r_{3}$ | $x_{4}$ | $x\left(A_{1}\right) \times\left(\mathbb{T}_{2}\right)$ |  |  |
| E | I | 0 | 0 | 0 | I 3 |  | 3 |
| $8 c_{3}$ | 2 | 2 | 2 | 2 | I 0 |  | 0 |
| $3 c_{2}$ | 0 | I | I | I | I I I |  |  |
| $6 \mathrm{~S}_{4}$ | 0 | 2 | 2 | 2 | I -I |  |  |
| $6 \sigma_{d}$ | 3 | I | I | I | I I |  | I |
|  | Rr 2 |  | T.I. 5 a |  |  |  |  |
| R | $\underline{r}$ | $r_{2}$ | $r_{3}$ | $r_{4}$ | $x\left(A_{1}\right) \quad x\left(T_{2}\right)$ |  |  |
| E | 0 | I | 0 | 0 | I 3 |  | 3 |
| $8 \mathrm{C}_{3}$ | 2 | 2 | 2 | 2 | I 0 |  | 0 |
| $3 c_{2}$ | I | 0 | I | I | I -I |  | I |
| $6 \mathrm{~S}_{4}$ | 2 | 0 | 2 | 2 | I -I |  |  |
| $6 \sigma_{8}$ | I. | 3 | I | I | I I |  | I |
| $\mathrm{Rr}_{3} \quad$ T.I. 50 |  |  |  |  |  |  |  |
| R | $r$ | $\mathrm{r}_{2}$ | $r_{3}$ | $r_{4}$ | $x\left(A_{1}\right) \quad x\left(\mathrm{~T}_{2}\right)$ |  |  |
| I | 0 | 0 | I | 0 |  | 3 |  |
| $8 c_{3}$ | 2 | 2 | 2 | 2 |  | 0 |  |
| $3 c_{2}$ | I | I | 0 | I |  | * I |  |
| $63_{4}$ | 2 | 2 | 0 | 2 |  | -I |  |
| $6 \sigma_{d}$ | I | I | 3 | I |  | I |  |

rotation $\frac{2 \pi}{3}$ around itself, it goes twice into $r_{2}$ under rotation $\frac{2 \pi}{3}$ ar ound $x_{4}$ and $-\frac{2 \pi}{3}$ around $r_{3}$ respectively etc.

We also include in the tables the characters of the representations of the $T_{d}$ group, which exist in the decomposition of the $\Gamma_{r} ;$ sinilarly tables are constructed for the rest of the coordinates $S_{2}=r_{2}, S_{3}=x_{3}$ etc. The tables for the rest coordinates are constructed using symetry considerations.

Using (I.I2),(I.I3) and (T.I.5), we get

$$
\begin{aligned}
& S_{I}\left(A_{I r}\right)=N \sum_{R} X_{A_{I}}(R) R r_{I} \\
& =N\left[X_{A_{I}}(E) r_{I}+X_{A_{I}}\left(C_{3}\right) 2 r_{I}+X_{A_{I}}\left(C_{3}\right) 2 r_{2}+X_{A_{I}}\left(C_{3}\right) 2 r_{3}+X A_{I}\left(C_{3}\right) 2 r_{4}\right. \\
& +\lambda_{A_{I}}\left(C_{2}\right) r_{2+} \lambda_{A_{I}}\left(C_{2}\right) r_{3}+\lambda_{A_{I}}\left(C_{2}\right) r_{4} \\
& +)_{A_{I}}\left(S_{4}\right) 2 r_{2}+\lambda_{A_{I}}\left(S_{4}\right) 2 r_{3}+\chi_{A_{I}}\left(S_{4}\right) 2 r_{4} \\
& \left.+\lambda A_{I}\left(\sigma_{d}\right) 3 r_{I}+\lambda_{A_{I}}\left(v_{d}\right) x_{2}+\operatorname{la}_{I}\left(\sigma_{d}\right) r_{3}+\gamma_{A_{I}}\left(\sigma_{d}\right) x_{4}\right] \\
& =6 N\left(r_{1}+r_{2}+r_{3}+r_{4}\right) \\
& =\frac{I}{2}\left(r_{I}+r_{2}+r_{3}+r_{4}\right)
\end{aligned}
$$

and similarly

$$
S_{I}\left(T_{2 r}\right)=\frac{1}{2 \sqrt{3}}\left(3 r_{I}-r_{2}-r_{3}-r_{4}\right)
$$

Since $T_{2}$ is a three dimensional representation there are two other partners $S_{2}\left(T_{2 x}\right)$ and $S_{3}\left(T_{2 x}\right)$ which have the same form as $S_{I}$ and are calcu lated using symetry considerations (simply we interchange cyclicly the Internal coordinates); these partners are tabulated in table 7 (T.T.7).

| T.I.6 |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $R$ | $\Theta_{I 2}$ | $\Theta_{I 3}$ | $\Theta_{I 4}$ | $\theta_{23}$ | $\theta_{24}$ | $\theta_{34}$ | $X\left(A_{I}\right)$ | $X(E)$ | $X\left(T_{2}\right)$ |
| $E$ | $I$ | 0 | 0 | 0 | 0 | 0 | $I$ | 2 | 3 |
| $8 C_{3}$ | 0 | 2 | 2 | 2 | 2 | 0 | $I$ | $-I$ | 0 |
| $3 C_{2}$ | $I$ | 0 | 0 | 0 | 0 | 2 | $I$ | 2 | $-I$ |
| $6 S_{4}$ | 0 | $I$ | $I$ | $I$ | $I$ | 2 | $I$ | 0 | $-I$ |
| $6 \sigma_{d}$ | 2 | $I$ | $I$ | $I$ | $I$ | 0 | $I$ | 0 | $I$ |

For the $I_{\theta}$ representation, choose $S_{I}=\theta_{I 2}$ and using the same procedure as for (T.I.5) we construct (T.I.6).

> Using then (I.I2),(I.I4) and (T.I.6) we get

$$
s\left(A_{I \theta}\right)=N \sum_{R} \lambda_{A_{I}}(R) R \theta_{I 2}-\frac{1}{\sqrt{6}}\left(\theta_{I 2}+\theta_{I 3}+\theta_{I 4}+\theta_{23}+\theta_{24}+\theta_{34}\right)
$$

For the two fold representation we calculate similarly the two partuers $S_{1}\left(E_{\theta}\right)$ and $S_{2}\left(E_{\theta}\right)$, where the second partaer is derived using coordinate $S_{2}=\theta_{I 3}$ and constructing table (T.I.6a) simply from(T.I.6) interchanging $\theta_{\mathrm{I} 2}, \theta_{I 3}$ and $\theta_{24}, \theta_{34}$.

Finally we derive the three partners $S_{I}\left(T_{2 \theta}\right), S_{2}\left(T_{2 \theta}\right)$ and $S_{3}\left(T_{2 \theta}\right)$ of the three dimensional representation which are tabulated in(T.I.7).

In the Table 7 we have excluded the redundant coordinate $S\left(A_{I \Theta}\right)$ (we must have one coordinate in the one diru representation).

The symmetry coordinates are not to be confused with the normal coordinates of the molecule, but they transform according to irredarepre sentations of the group. They also do not diagonalize the secular equation that gives the eigenfrequencies, but if K.E and P.E are expressed In terns of them, the determinant appears in block form, each correspond ing to certain representation of dimension equal to the number of linear independent symmetry coordinates associated with that representation.

The two modes $T_{2}(r)$ and $T_{2}(\theta)$ are actually mixed in the sense that the molecule does not vibrate according to symetry coordinates cor responding to $T_{2}(r)$ and $T_{2}(\theta)$ but acce to a motion which is a Iinear combination of these two. The frequency of vibrations can be found ky solving the eigenvalue problem for each block.

## T.I. 7

SIMRETRY COORDINATES FOR METHANE XX ${ }_{4}$

$$
\begin{aligned}
& A_{I}(r)=S\left(A_{I r}\right)=\frac{I}{2}\left(r_{I}+r_{2}+r_{3}+r_{4}\right) \\
& T_{2}(r)=S\left(T_{2 r}\right)=\left\{\begin{array}{l}
\frac{1}{2 \sqrt{3}}\left(3 r_{I}-r_{2}-r_{3}-r_{4}\right) \\
\frac{1}{2 \sqrt{3}}\left(3 r_{2}-r_{I}-r_{3}-r_{4}\right) \\
\frac{1}{2 \sqrt{3}}\left(3 r_{3}-r_{I}-r_{2}-r_{4}\right)
\end{array}\right.
\end{aligned}
$$

$A(\theta)$ redundant

$$
\begin{aligned}
& E(\theta)=S\left(E_{\theta}\right)=\left\{\begin{array}{l}
\frac{1}{2 \sqrt{3}}\left(2 \theta_{I 2^{-}} \theta_{I 3^{-}} \theta_{I 4}-\theta_{23}-\theta_{24}+2 \theta_{34}\right) \\
\frac{1}{2 \sqrt{3}}\left(2 \theta_{I 3^{-}}-\theta_{I 2}-\theta_{I 4}-\theta_{23}-\theta_{34}+2 \theta_{24}\right)
\end{array}\right. \\
& T_{2}(\theta)=S\left(T_{2 \theta}\right)=\left\{\begin{array}{l}
\frac{1}{\sqrt{2}}\left(\theta_{I 2}-\theta_{34}\right) \\
\frac{1}{\sqrt{2}}\left(\theta_{I 3^{-}}-\theta_{24}\right) \\
\frac{1}{\sqrt{2}}\left(\theta_{I 4}-\theta_{23}\right)
\end{array}\right.
\end{aligned}
$$

## CHAPTER II

MOLECULAR FIELD APPROXIHATION METHOD
INTRODUCTION
The purpose of this,is to develop and discuss a method known as "molecular field approxtmation" or "internal Rield approximation"which is elegant in describing the rotational states in molecular crystals oí linear molecules.

The MFA is appropriate when one wants to find a first approxima tion to a fresh crystal statistical problem such as ours which has not been solved before. Tc do this, we must know the explicit form of the rotational wave functions of a freely rotating molecule.

The results of this method applied to ortho-hydrogen(J=I) byJames \& Raichg in Nitrogen by PoDunmore and methane by Yamanoto. ${ }^{(41)}$

Through NFA method we shall try to compute all the themodymami cal quantities of the systern under consideration.

Before we develop the method, we do the necessary approximations i) Since librational modes are studied, we consider the centers of mass of the nolecules fixed at the lattice sites, so there is no translation al motion. ii) We ignore the electrons completely due to the fact that there are in their ground states; actually since at $\operatorname{Tr} 20^{\circ} \mathrm{K}, \mathrm{KT} \sim 10^{-4} \times 20$ $\sim .002 e v$ and for Hydrogen the energy which must be given from outside to excite an electron from its ground state ( $n=I$ ) to ( $n=2$ ) is $16.33 \times$ $\times I 0^{-19}$ erg. $\sim I C e v$, then we are excused to make this assumption even at room temperature $\mathrm{KT} \sim \mathrm{IO}^{-4} \times 300 \sim .03$ ev.

Description of the systen :
After all assumptions, we finally consider a system of rigid iota tors representing the molecules of any arystal with their centers of mass fixed at the points of a risid lattice (no vibrations).

To describe the orientation of molecule igat site $i_{\text {g }}$ since we are concemed with rotations ; the position of the molecules and their interac tion is going to be given in terms of angular coordinates.

The orientation of the $i^{\text {th }}$ molecule is given by its polar angle $\left(\theta_{i}, \varphi_{i}\right)=\omega_{i}$ of the internuclear axis with the polar axis taken to the equilibrium direction $\theta_{1}=0$ (fig. 7). The interaction consequently of the $i^{\text {th }}$ and $j^{\text {th }}$ molecules, will be represented by a potential function which will be a function of the angular coordinates of their orientations.

The Hamiltomian therefore of the system will be writen as :

$$
\begin{equation*}
H_{s}=\sum_{i}^{N} H_{j}\left(\omega_{i}\right)+\frac{I N}{2} \sum_{i}^{N} \sum_{j}^{N} \nabla_{i j}\left(\omega_{i}{ }^{g} \omega_{j}\right) \tag{II.I}
\end{equation*}
$$

where $H_{i}\left(L_{i}\right)$ is the rotational $K$.E operator of the $i^{\text {th }}$ molecule, $V_{i j}$ the potential energy of the interaction of the molecules $i$ and $j$ depending on the direction of the intermolecular axis.

We shall employ here a quantum mechanical treatment of the prob 1eng.

Construction of the density matrix : Any quantum mechanical ensemble con sisting of $\mathbb{K}$ systems is represented by a density matrix ( or density $f^{n}$ in classical mechanics) .

Assume that each nolecule $i$ can occur in states $Y_{m}^{i}\left(i_{i}\right)$ where $m$ $=1,2,3,0$ are states of a single nolecule which form an orthogonal set of functions with probability of occureace of state $p: p_{r a}^{j}$ for the $i^{\text {th }}$ mo
lecule.
This probability is independent of $p_{n}^{j}$ for $i \neq j$, that is, the probability is independent of the state in which another molecule $j$ may be in the crystal, so the one molecule density matrix is writen by definition:

$$
\begin{equation*}
P_{i}=\sum_{\text {III }}|m\rangle p_{m}^{i}\langle m| \tag{II.2}
\end{equation*}
$$

where we surn all over the possible states available to the molecule $i$ and every state multiplied by the probability of its occurence. Since $p_{m}^{i}$ is independent of $p_{n}^{j}$ then the total wave $f^{n}$ of the whole crystal can be writen in product form :

$$
\begin{equation*}
\Psi_{\{m\}}=\prod_{i=1}^{N} \Psi_{m_{i}} \tag{II.3}
\end{equation*}
$$

where $\{m\}$ denotes the set of the quantum numbers $m_{I}, m_{2}, \ldots$ that specifies the $\psi^{\prime \prime}$ s for individual molecules. By the same arganent $\Psi_{\{m\}}$ describes the state of the crystal with probability:

$$
\begin{equation*}
P_{\{q\}}=\prod_{i=1}^{N} p_{m}^{i} \tag{II.3a}
\end{equation*}
$$

which is the probability that the crystal is in state $Y$ Y in $^{\circ}$. The density matrix of the crystal consisting of molecules will be:

$$
\begin{equation*}
P=\sum_{\left\{m_{\xi}\right\}}\left|m_{I} m_{2} \cdot \cdot m_{N}\right\rangle P_{\left\{m_{\xi}\right.}\left\langle m_{I} m_{2} \cdot \cdot m_{N}\right| \tag{II.4}
\end{equation*}
$$

The assumption of statistical independence (II.3a) allows is to factorize the density matrix of the crystal as a product of individual mo lecule density matrices(II.2):

$$
F=\sum_{m}\left|m_{I} m_{2} \ldots m_{\mathbb{N}}\right\rangle \prod_{i} p_{m_{i}}^{i}\left\langle m_{I} m_{2} \ldots m_{N}\right|
$$

$$
\begin{align*}
& =\prod_{i}\left(\sum_{n_{i}}\left|m_{i}\right\rangle p_{m_{i}}{ }^{i}\left\langle m_{i}\right|\right) \\
& =\prod_{i}^{N} \mid p_{i} \tag{II.5}
\end{align*}
$$

where $P_{i}=\sum_{m_{i}}\left|m_{i}\right\rangle p_{m_{i}}^{i}\left\langle m_{i}\right| \quad$ is the one molecule dersity matrix.
Rean field potentiai: The total potential at the position of the $i^{\text {th }}$ mole cule due to all other molecules, or the potential energy of the $i^{\text {th }}$ mole cule is

$$
\begin{equation*}
\nabla^{j}\left(\omega_{i}\right)=\sum_{j} \sum_{\substack{n \\ j \neq i}}\left\langle\left.\psi_{n}^{j}\right|_{i j} \mid \psi_{n}^{j}\right\rangle p_{n}^{j} \tag{II.6}
\end{equation*}
$$

Energy calculation : The average energy of the system associated with $\bar{\Psi}\{m\}^{\text {when }} j^{\text {th molecule }}$ is in state $m_{i}$ and $j^{\text {th }}$ molecule in state $m_{j}$ whi ch of course are orthogonal states is

$$
\begin{align*}
\langle H\rangle_{m_{i}} & =\left\langle\psi_{m_{i}}^{i}\right| \sum_{i} H_{i}\left|\psi_{m_{i}}^{i}\right\rangle+\frac{1}{2} \sum_{i j}\left\langle\psi_{m_{i}}^{i} \psi_{m_{j}}^{j}\right| V_{i j}\left|\psi_{m_{i}}^{i} \psi_{m_{j}}^{j}\right\rangle \\
& =\sum_{i} w_{m_{i}}^{i}+\frac{1}{2} \sum_{i j} w_{i m_{i} m_{j}}^{i j} \tag{II.7}
\end{align*}
$$

where $w_{m}^{i}=\left\langle\psi_{m}^{i}\right| H_{i}\left|\psi_{m}^{i}\right\rangle$
is the rotational energy of the $i^{\text {th }}$ molecule in state $m$, and

$$
\begin{equation*}
w_{m n}^{i j}=\left\langle\psi_{m}^{i} \psi_{n}^{j}\right| v_{i j}\left|\psi_{m}^{i} \psi_{n}^{j}\right\rangle \tag{II.9}
\end{equation*}
$$

is the interaction potential energy of the $i^{\text {th }}$ and $j^{\text {th }}$ molecules in sta tes in and $n$ respectively (where we have rejected the subscripts of $m_{i}$, since II. 8 and II. 9 hold for any state of the set $\{m\}$ ).

The intemal energy of the crystal mill be a sumation over all the possible states multiplied by the piobability of their occurence in
the sum:

$$
\begin{align*}
E & =\sum_{\{m\}}\langle H\rangle_{\{m\}} P_{\{m\}} \\
& =\sum_{i m} W_{m}^{i} P_{m}^{i}+\frac{1}{2} \sum_{i m} \sum_{i n} W_{m n}^{i j} P_{m}^{i} P_{n}^{j} \tag{II.IO}
\end{align*}
$$

Use now the fact that $\langle H\rangle=\sum{ }_{m} \mathrm{p}_{\mathrm{n}}=\operatorname{Tr} \mathrm{TH}^{H}$, the proof is as fol Lows:

$$
\operatorname{TrpH}=\operatorname{Tr}\left[\left(\sum_{m}|m\rangle P_{m}\langle m|\right) H\right]=\sum_{m} P_{m} \operatorname{Tr} \Pi_{m} H \quad \text { where }|m\rangle\langle m|=\prod_{m}
$$

is the projection operator the square of which is the unity operator and its trace untty, therefore

$$
\begin{aligned}
\operatorname{Tr} \rho H & =\sum_{m} P_{m} \operatorname{Tr} \Pi_{m}^{2} H=\sum_{m} P_{i n}\left(\operatorname{Tr} \Pi_{m} H \Pi_{m}\right) \\
& =\sum_{m} P_{m}\left[T_{r}|m\rangle\langle m| H|m\rangle\langle m|\right]=\sum_{m} P_{m}\langle m| H|m\rangle=\sum_{m} P_{m} W_{m} Q_{0} E_{c} D
\end{aligned}
$$

Combining (II.IO),(II.9) and (II.8) we get

$$
\begin{equation*}
E=\sum_{i}\left(t_{r}{ }^{(i)} F_{i} H_{i}+\frac{1}{2} \sum_{i \neq j} t r^{(i)} t r^{(j)} V_{i j} F_{i} F_{j}\right) \tag{II.II}
\end{equation*}
$$

which is the total energy of the crystal, where ir ${ }^{(i)}$ is the trace over the Hilbert space of the $i^{\text {th }}$ nolecule.

The total energy of the $i^{\text {th }}$ rolecule is:

$$
\begin{equation*}
E_{i}=\left\langle E_{i}\right\rangle+\sum_{j} \operatorname{tr}^{(j)} V_{i j} \rho_{j} \tag{II.IIa}
\end{equation*}
$$

Thermociynamics : We can now define as operator which instead of being multiplicative is additive, namely In $p$. This operator has the advantage of being extensive for a large ensemblé ioe proportional to the no of constituent systems). For a uniform thermodyname ensemble, this inplies
proportionality to the voluke.
The average value of $\ln p,\langle\ln p\rangle=t r p \ln p$ aside from coastant it is called the Entrogy $S$ of the system: $S=-k$ tr pla $\rho$ (IIoI2) where



The most important density matrix in physies is the one describ Ing a system in themal equilibriwn with the surcoundings at Temperat. To

The entropy at equilibrium $S \rightarrow S_{\text {max }}$ and the iree energy $F \rightarrow F_{\text {min }}$ so $\mathrm{F}_{\min }=\mathrm{E} \mathrm{TS}_{\text {max }}$ at equilibrium in tewperature $T$.

Prinimiziag the above expression wotot fi we can find the 80 m of the density matrix which describes the systen in equilibrium at terap .

Solving the variatiomal problem, we get the form of $f_{i}$ to be:

$$
\begin{equation*}
\rho_{i}=\frac{e^{-b E_{i}}}{Z_{i}} \tag{0}
\end{equation*}
$$

where $Z_{i}=t r^{(i)} e^{-\hat{C E}_{i}}$, and using (II.IIa) the eqn(II.I4) becomes

$$
\begin{equation*}
P_{i}=\frac{e^{-\ell\left[H_{i}+\sum_{j} \sum_{r}^{(j)} V_{i j} F_{j}\right]}}{t_{1}^{-(i)} e^{-6\left[H_{i}+\sum_{j} t r^{(i)} V_{i j} F_{j}\right]}} \tag{II.I5}
\end{equation*}
$$

Equation (II.6) is written $U^{i}\left(\omega_{i}\right)=\sum_{j}\left\langle V_{i j}\right\rangle$ by definition of the mean ralue and since $\left\langle V_{i j}\right\rangle=\operatorname{tr}^{(i)}{ }^{(i)} V_{j} V_{i j}$ then:

$$
\begin{equation*}
\tilde{U}^{i}\left(\cos _{j}\right)=\sum_{j} i x^{(j)} F_{j} V_{i j} \tag{IT,I6}
\end{equation*}
$$

and by (II.I5)
so (II.I6) becomes

$$
\begin{equation*}
\left\langle H^{i}\right\rangle=\sum_{j} \operatorname{tr} r^{(j)}\left(1 / e_{j}\right) e^{-6\left[H_{j}+U_{j}\right]} \tag{0}
\end{equation*}
$$

and the internal energy (II.II) is written

$$
\begin{equation*}
E=\sum_{i} t r^{(i)} H_{i} \rho_{i}+\frac{1}{2} \sum_{i} t r^{(i)} \rho_{i} \tilde{U}_{i} \tag{II.I9}
\end{equation*}
$$

in terms of molecular field potential.
Entropysfree energy: Using eau (II.I2)

$$
\begin{align*}
s & =-k \operatorname{tr} \rho \ln \rho=-k \operatorname{tr} \rho \sum_{i} \ln \rho_{i} \quad \text { by }(I J .53) \\
& =-k \operatorname{tr} \rho \sum_{i}\left[-b E_{i}-\ln Z_{i}\right] \quad \text { where } \quad E_{i}=\sum_{m} \epsilon_{i m} \Pi_{i m} \\
& =k \operatorname{tr} \rho \sum_{i} E_{i}+k \operatorname{tr} \rho \sum_{i} \ln Z_{i} \\
& =\frac{1}{T} \operatorname{tr} \rho \sum_{i m} \epsilon_{i m} \Pi_{i m}+k \ln Z \quad \text { since } \operatorname{tr} \rho=1 \text { and } Z=\prod_{i} Z_{i} \\
& =\frac{1}{T} \sum_{i m} \epsilon_{i m}\left\langle\eta_{i m}\right\rangle+k \ln Z \quad(I I .20) \tag{II.20}
\end{align*}
$$

where ir $\rho n_{i n}=\left\langle n_{i m}\right\rangle$ and $\left\langle n_{i m}\right\rangle=\frac{I}{e^{n_{i m}-I}}$ and using $\sum_{i m} \epsilon_{i m}=\sum_{i} E_{i}$
$=\sum_{i}\left(\tilde{H}_{i}+\tilde{U}_{i}\right)$ we get finally:

$$
\begin{equation*}
S=\sum_{i}=\frac{I}{T}\left(\tilde{H}_{i}+\tilde{U}_{i}\right)+k \ln Z \tag{II.2I}
\end{equation*}
$$

in temp of molecular field.
Free energy is defined as $F=E-T S$, so using (II.I9)

$$
\begin{align*}
F & =\sum_{i} t^{(i)} H_{i} \rho_{i}+\frac{1}{2} \sum_{i} t r^{(i)} p_{i} \tilde{U}_{i}-\sum_{i} \tilde{H}_{i}-\sum_{i} \tilde{U}_{i}-k T \ln Z \\
& =\operatorname{lkT} \operatorname{In} Z=\frac{I}{2} t r^{(i)} \rho_{i} \tilde{U}_{i} \quad\left(I I_{0} 22\right) \tag{0}
\end{align*}
$$

Mean deviation angle: By definition the MDA matrix element is

$$
\begin{equation*}
\left\langle\theta_{\mathrm{k}, \mathrm{~m}}\right\rangle^{(J)}=\left\langle\psi_{\mathrm{kJm}}^{(J)}\right| \theta^{2}\left|\psi_{\mathrm{k}, \mathrm{~m}}^{(J)}\right\rangle \tag{II.23}
\end{equation*}
$$

where $k=X_{s} y, z$ refers to space ined axes (SFA), $m=X, Y, Z$ refers to mo lecule fired axes (MFA), $\theta_{k,}$ refers to angle between the components of SFA and $\mathrm{MFA}_{\text {s }} \psi_{\mathrm{k}, \mathrm{m}}(J)$ are the explicit rotational wave functions of the freely rotating molecule and $\left\langle\Theta_{l n, \text { nin }}^{2}\right\rangle$ denotes the mean square deviation of the molecular aris from its equilibriun orientation which has taken to be when the SFA and MFA coincide (fig.8).

Employing cosine functions,using trigonometric expansionswe get (rejecting higher than $2^{\text {nd }}$ order terras ) : $\left\langle\cos ^{2} \theta\right\rangle=I-\left\langle\theta^{2}\right\rangle$ and (II.23) becomes

$$
\left.\left\langle e_{k, m}^{2}\right\rangle^{J}\right) \approx I-\left\langle\Psi_{k, n}^{(J)}\right| \cos ^{2} \theta\left|\Psi_{k, m}^{(J)}\right\rangle \quad \text { (II.24) }
$$

Application to methane (free molecule): Since we know the explicit form of the rotational wave functions of a freely rotating molecule, as has been calculated and tabulated by Yamanoto and Kataoka, we can calculate the $\operatorname{lDA}$ using eqn (II. 24 ).

We write down the explicit rotational wave sunctions taken from Tamamoto:

$$
\begin{align*}
& \Psi_{k, m}^{(J)}=\frac{1}{\sqrt{2}}\left[(2 J+I) / 8 \pi^{2}\right]^{\frac{1}{2}}\left\{D _ { - k , m } \left(J D_{k, m}(J)\right.\right.  \tag{IT.25}\\
& \Psi_{0, m}^{(J)}=\left[(2 J+I) / 8 n^{2}\right]^{\frac{1}{2}} D_{D_{s} m}(J)(x, \dot{b}, J) \tag{II.26}
\end{align*}
$$

special case when $k=0, D(x, h, \gamma)$ are the rotational matrices, whieh are sunctions of the Euler's angles thru which the molecule has been rota ted fron its standard orientation.

To calculate the $M$, we can also use the relations given between
the rotational matrix elements and the spherical harmonics, taking the phase convention into account.

Using ROSE (Angular momentum theory) we find the relation of rotational matrix to spherical harmonics, for the special case $k$.

$$
\begin{equation*}
D_{0, \mathrm{~m}}^{(J)}(\alpha, b, y)=\left[\frac{4 \Pi}{2 J+I}\right]^{\frac{1}{2}} \mathbb{X}_{J m}^{*}(b, \alpha) \tag{II.27}
\end{equation*}
$$

For the case $k=0$, eqn(II.24) becomes

$$
\begin{equation*}
\left\langle\theta_{0, \mathrm{~m}}^{2}\right\rangle=I-\left\langle\psi_{0, \mathrm{~m}}^{(J)}\right| \cos ^{2} \theta\left|\psi_{0, \mathrm{~m}}^{(J)}\right\rangle \tag{II.28}
\end{equation*}
$$

where now $\Theta_{O_{0}}$ refers to the angle between the $z$ and $Z$ axes of the two systems. Substituting (II.26),(II.27) into (II.28) we get

$$
\left\langle\Theta_{0, \mathrm{~m}}^{2}\right\rangle^{(J)} I-\left\langle\left.\mathrm{Y}_{\mathrm{Jm}}\right|^{\cos ^{2} \theta\left|Y_{J m}\right\rangle}\right.
$$

where we integrated over $\gamma$ which contributes $2 \pi$ to the integral and since (I I.27) is independent of $\gamma$, we set $\gamma=0$ arbitrarily.

For the case $k=0$, a practical method to verify our results is to sum for a specific $J$, all over the matrix elements for the $2 J+I$ diffferment values of $m_{8}$ so

$$
\sum_{m=-J}^{J}\left\langle\psi_{0, m}^{J}\right| \cos ^{2} e\left|\psi_{c, m}^{J}\right\rangle=\int_{0}^{2 \pi} d \gamma \int_{0}^{2 \pi} d \varphi \int_{0}^{\pi} \cos ^{2} \theta \sin \theta d \theta\left(\sum_{m=-J}^{J}\left|\psi_{0, m}^{J}\right|^{2}\right)
$$

$$
\begin{equation*}
=1 / 3(2 J+1) \tag{II,30}
\end{equation*}
$$

since $\sum_{m=-J}^{J}\left|\psi_{c_{1} m}^{J}\right|^{2}=\frac{2 J+1}{8 \pi^{2}}$ and $\sum_{m=-J}^{J}\left\langle\Theta_{0, m}^{2}\right\rangle^{J}=\frac{2}{3}(2 J+1) \quad$ (I I.3O)
We calculate now the different 1 DA for $\mathrm{J}=0, \mathrm{I}_{\mathrm{g}} 2$.
$J=0, m=0$

$$
\left\langle\Theta_{0,0}^{2}\right\rangle^{J=0}=I-\left\langle Y_{00}\right| \cos ^{2} \theta\left|Y_{00}\right\rangle=I-0.333=0.667
$$

$J=I_{9} m= \pm I_{8} 0$
Matrix elements: $\left\langle\mathrm{Y}_{\mathrm{IO}}\right| \cos ^{2} \theta\left|\mathrm{Y}_{I O}\right\rangle=0.6$

$$
\left\langle I_{I, \pm I}\right| \cos ^{2} \theta\left|Y_{I,+I}\right\rangle=0.2
$$

So

$$
\begin{aligned}
& \left\langle e_{c, c}^{2}\right\rangle^{J=1}=0.4 \mathrm{rad} \\
& \left\langle e_{c_{1} \pm 1}^{2}\right\rangle^{5=1}=0.8 \mathrm{rad} .
\end{aligned}
$$

and $\sum_{\substack{1=-1}}^{i}\left\langle Y_{1 m}\right| \cos ^{2} \theta\left|Y_{1 m}\right\rangle=1, \sum_{m=-1}^{1}\left\langle\Theta_{0, m}^{2}\right\rangle^{J=1}=2$
$J=2, m= \pm 2, \pm I, 0$
Matrix elements: $\left\langle X_{2,2}\right| \cos ^{2} 0\left|X_{2}+2\right\rangle=0.14 \mathrm{I}$

$$
\begin{aligned}
& \left\langle V_{2, \pm}\right| \cos ^{2} 0\left|Y_{2}+I\right\rangle=0.427 \\
& \left\langle V_{2,0}\right| \cos ^{2} 0\left|Y_{2,0}\right\rangle=0.523
\end{aligned}
$$

So $\left\langle\theta_{0,0}^{2}\right\rangle^{3 * 2}=0.477 \mathrm{rad}$
$\left\langle\Theta_{c, \pm 1}^{3}\right\rangle^{9=2}=0.572 \mathrm{rad}$.
$\left\langle\Theta_{0,2}^{2}\right\rangle^{5 \div 2}=0.858 \mathrm{rad}$.



Molecule at equilibrium.
fig. 7


Equilibrium orientation of $\mathrm{CH}_{4}$ molecule, when IFA and SFA ares coincide.


Molecule rotated at aggles $\theta$ and $\varphi$ iron equilibriun.


Holecule rotated

## CHAPTER III

NUCLEAR SPIN WAVE FUNCIIONS FOR METHANE

Nuclear spin wave furctions $X\left(\right.$ IM $\left._{I}\right)$, where $I$ is the total nuclear spin of the nolecule and $\mathrm{K}_{\mathrm{I}}$ is the component of the above vector on $\mathrm{z}^{\prime}$ axis of the $\mathrm{SFF}_{8}$ these axe obtained by Clebsch-Gordon method by decomposing the system into constituents and then coupling the angulax momenta of the constitu ent parts.

I, operator, obeys the eigenvalue equations

$$
\begin{aligned}
& I^{2}\left|I M_{I}\right\rangle=I(I+1)\left|I M_{I}\right\rangle \\
& I_{Z^{\prime}}\left|I M_{I}\right\rangle=M_{I}\left|I M_{I}\right\rangle
\end{aligned}
$$

The coubined vibrational and nuclear spin functions $\chi\left(B \xi, I M_{I}\right)=\chi(6 \xi)$ $\chi\left(\mathrm{IM}_{\mathrm{I}}\right)$, where $\chi(6 \xi)$ is the vibrational part, are obtained taking into consi= deration how the vibrational modes transfom( paxt I). Here $b$ denotes the set of representations of the methane group,according to which the differ ent vibrational nodes $\xi=x_{s} J_{g} z$ transform and we have found then to be $B=A_{I}$ $\mathrm{T}_{2}, \mathrm{E}$ (T.I. 3 ) 。

To construct the spin wave functions for methane, we separate the systern (molecule) into two Hydrogen molecules and then combine the wave fu nctions of these, acce to rules of addition of angular momenta.

There are three different vays of partitioning the four $H$ atoms into two Hydrogen molecules; that is atoms lying on planes perpedicular to $x$ axis $(I, 3)$ and $(2,4)$, on planes perpedicular to $y$ axis $(I, 4)$ and $(2,3)$ and perpedicular to $z$ axis $(I, 2)$ and $(3,4)$ having wave functions $\left.\left.\mid I_{I} 3 I_{1}\right]\right\rangle$ $\left|I_{2,4} m_{2,4}\right\rangle$ and so on.

Since $I_{i j}=I_{8} O$ for the Hydrogen molecules ${ }^{2}$ then the total I satis fying the condition :

$$
\left|I_{I_{, 3}}-I_{2,4}\right| \leqslant I \leqslant\left|I_{I, 3}+I_{2,4}\right|
$$

must have values $I=2,1,0$ 。
Detailed symetry arguments show how the vibrational fumctions and muclear spin fuactions must be combined（ as it was mentioned before）in order to preserve the overall sympetry of the wave function undex the ope rations of the group ${ }^{2}$ ．The result is：

$$
\begin{aligned}
& \left.X\left(\mathrm{~T}_{2} x_{2} 1_{0} m_{I}\right) \text { o } X\left(\mathrm{~T}_{2} y_{2} 1 \mathrm{~m}_{I}\right) \cdot X\left(\mathrm{~T}_{2} z_{2} 1 \mathrm{~m}_{I}\right)\right) \\
& \chi(E 1,00) \quad \therefore \chi^{(E 2,00)} \\
& \text { and } X\left(A_{I}, 2 m_{I}\right)
\end{aligned}
$$

Denote with $a_{s}$ spin up state and with $b$ ，spin down state of the indi vidual atoms ${ }_{8}$ so $a_{i}, b_{i}$ where $i=1,2_{8}, 3,4$ are the up and down spin states of the four $H$ atoms：therefore the states $\left|I_{s} M_{I}\right\rangle$ are the following，for $I=2$ ， $|22\rangle,|21\rangle,|20\rangle,|2-1\rangle,|2-2\rangle$, for $I=1,|11\rangle,|10\rangle,|1-1\rangle$ and for $I=0$ the $|00\rangle$ ．

The state $|22\rangle$ arises when all spins are up，so we choose

$$
\begin{equation*}
|22\rangle=\prod_{i=1}^{4} a_{i}=a_{I} a_{2} a_{3} a_{4} \tag{III.2}
\end{equation*}
$$

Introduce the Operators

$$
\begin{equation*}
I_{ \pm}=I_{I}+I_{2}+I_{3}+I_{4} \tag{III.4}
\end{equation*}
$$

obeying the kown rules

$$
\begin{equation*}
I+\left|M_{I}\right\rangle=\left[I(I+1)-l_{I}\left(M_{I}+1\right)\right]^{\frac{1}{2}}\left|I_{s} H_{I}+1\right\rangle \quad \text { (III。4) } \tag{III.5}
\end{equation*}
$$

where $I_{i}{ }^{m} a_{i}=b_{i}$ and $I_{i}{ }^{m} b_{i}=0$
Starting from $|22\rangle$ we derive all the others，operating on（III。2） with the Loweriag operator（III．4）and taking ixto consideration（III．3．5）

So:

$$
I_{-}|22\rangle=[I(I+1)-M(M-1)]^{\frac{1}{2}}|2 I\rangle=2|2 I\rangle
$$

and $|2 I\rangle=\frac{1}{2} I_{-}|22\rangle=\frac{1}{2}\left(I_{I}^{-}+I_{2}^{-}+I_{3}^{-}+I_{4}^{-}\right)\left(a_{I} a_{2} a_{3} a_{4}\right)$, and using (III.5) we get $|2 I\rangle=\frac{1}{2}\left(b_{1} a_{2} a_{3} a_{4}+a_{I} b_{2} a_{3} a_{4}+a_{I} a_{2} b_{3} a_{4}+a_{I} a_{2} a_{3} b_{4}\right)$ and Lowering again we construct the rest four wave functions for $I=2$ which are tabulated in table (T.III.I) and are properly normalized.
${ }^{(42)}$ We caiculate now the functions for $I=1$, which will be orthogonal to functions $\left|2 M_{I}\right\rangle$, so it must be $\langle 2 I \mid I I\rangle=0$. A function orthogonal to $|2 I\rangle$ will be one derived simply by inspection, having the same form as $|2 I\rangle$ but in which we have interchanged the signs of the terms; thus $|11\rangle=\frac{1}{2}\left(b_{I} a_{2} a_{3} a_{4}-\right.$ $-a_{I} b_{2} a_{3} a_{4}+a_{1} a_{2} b_{3} a_{4}-a_{1} a_{2} a_{3} b_{4}$ ) and using lowering operators again we obtain the rest two functions, which are tabulated in(T.III.I), where in $|I-I\rangle$ we have changed the signs all over, to bring it to the same form as the $|I I\rangle$ (only $a$, and $b$,having been interchanged).

Here since $T_{2}$ representation is threefold we have three set of fu nctions $\left(T_{2 x}, T_{2 y}, T_{2 z}\right)$, that is, another two set of triplets; these sets can be obtained by using symmetry considerations,interchanging the signs of the terms and finally tabulate in (T.III.I) (In $|11\rangle, \|-1\rangle$ we interchange simply the roles of $a$, and $b$ ).

By inspection we see that these are not antisymetric under on ar bitrary interchange of two nuclei; e.g $1 \leftrightarrow 2$ in the function $\frac{1}{\sqrt{2}}\left(b_{1} a_{2} b_{3} a_{4}-\right.$ $\left.-a_{1} b_{2} a_{3} b_{4}\right)$ gives $\frac{1}{\sqrt{2}}\left(a_{1} b_{2} b_{3} a_{4}-b_{1} a_{2} a_{3} b_{4}\right)$ which is one of the other $||0\rangle$ functions with interchanged sign.

So we see that spin triplets are neither symmetric nor antisymmet ric under interchange of two protons.

We form now the singlet wave functions ior $I=0$, we require two
sets of singlet states for the $E$ representation, $X(51,00)$ and $X(E 2,00)$. We construct them again by inspection using orthogomality conside rations of $|00\rangle$ and $|10\rangle,|20\rangle:$ me therefore choose $|00\rangle$ to have exactly the sane form with the $|20\rangle$ with coexicienis which will be calculated,us Ing the fact that $|00\rangle$ must be orthogonal to $|10\rangle$ and $|20\rangle$ functions. So

$$
\begin{aligned}
|00\rangle=\frac{1}{\sqrt{6}}\left\{c_{1}\left(a_{1} a_{2} b_{3} b_{4}+b_{1} b_{2} a_{3} a_{4}\right)\right. & +c_{2}\left(a_{1} b_{2} a_{3} b_{4}+b_{1} a_{2} b_{3} a_{4}\right)+c_{3}( \\
& \left.+c_{3}\left(a_{1} b_{2} b_{3} a_{4}+b_{1} a_{2} a_{3} b_{4}\right)\right\}
\end{aligned}
$$

The conditions $\langle 00 \mid 20\rangle=\langle 00 \mid 10\rangle=0$ and $\langle 00 \mid \nu 0\rangle=1$ give us the two siaglet eigerfuactions which are found togeture with the others in (T.III.I) These two siaglet functions are mutually orthogonal.

VIBRATIOTAI-NUCLBAR SPIN WAVE FUNGOIONS FOR THE METHANE MOLECULE


IMFRA RED AND RAUAM SPECTRA AMD STRUCTURES OF CRYSTALITME

## PHASES OF METHANE

## IITRRODUCTIOR

Crystaline methane is inown to have two phase changes at $20.4^{\circ} \mathrm{K}$ passing from phase I to phase IIg and at $8^{\circ}{ }^{\circ} \mathrm{E}$ passing to phase III for $\mathrm{CH}_{4}$; the same happens for $\mathrm{CD}_{4}$ at $270 I^{\circ} \mathrm{K}$ and $22.2^{\circ} \mathrm{K}$ respectively.

Specilicmeat strdies show these to be $\mathrm{K}_{\text {-trpe }}$ transitions and an expianation is that they nesult from changes in molecular orientation

This conclusion is also supported by detailed studies of the Intra red and Ramadi spectra.

It is these latter strdies which we shall discuss in the present chaptes.

Spectra from crystalline phases of methane:
It is known that an EM wave (radiation) falling on a molecule or solid can induce transitions from one stationary state to another thru couplo ing with either the dipole moment $\mu$ (IR transition), or the polarizabili ty $\alpha$ (Raman induced transition) components. These effects are used to its vestigate the vibrational energy levels of a molocule or solid and tell its structure.

The selection rules fmpose the condition that a transition between energy levels (i.e tronsition from one normal mode to another) is possible if the matrix elements $\langle m| n|n\rangle$ differ from zero, where $p=x, y, z$, $x^{2}, y^{2}, z^{2}, x y, y z, z x$ etc iss an operator corresponding to the physical influence causing the transition from one state $\psi_{m}$ to another $\psi_{n}$ depending upon the case.

These integrals are different from zero is comparing the di rect products of $\psi_{n}$ and $\psi_{m}$ with the symmetry species of $p_{\text {, }}$ have

$$
I_{\mathrm{p}} \subset I_{\psi_{\mathrm{H}}} \times I_{\psi_{\mathrm{n}}}
$$

Transition $\psi_{n} \rightarrow \psi_{m}$, where $n$ and $n$ repiesent a set of quantum numbers de
 for infra red and $\langle n| x|m\rangle \neq 0$, i.e $I_{A_{I}} \in I_{\psi_{n}} x I_{x} \times I_{H_{m}}$ for Raman induced ira nsitions, where $x$ is the polarizability and $\mu$ the dipole noment.

All these selection rules are only valid for a molecule in field free space, that is,one in which no external EM forces are acting ex cept the interaction with the light bean. The effects of the external for
ces are even noticeable in the gas phase when the pressure is increased and normally forbidden transitions become IR active ${ }^{(i)}$

We have also great differencies between gas,solid and liquid spec tra noticed by Anderson and Savoie. (6) The frequencies of vibration are also very dependent upon the solvent inediufic (i4)

The normal modes of tetrahedral $\mathrm{XI}_{4}$, which were calculated in $I_{\text {. }}$ transform as the following representations of $T_{d}$ :

| $Q_{I}$ | $\underbrace{Q_{2}, Q_{3}}$ | $Q_{4}, Q_{5}, Q_{6}$ | $\underbrace{Q_{7}, Q_{8}, Q_{9}}$ |
| :---: | :---: | :---: | :---: |
| ${ }^{A_{I}}$ | E | $\mathrm{T}_{2}$ | $\mathrm{T}_{2}$ |
| $\alpha_{x x}+\alpha_{y y}+\alpha_{z z}$ | $\begin{aligned} & \alpha_{x x}-\alpha_{y y} \\ & 2 \alpha_{z z}-\alpha_{x x}-\alpha_{y y} \end{aligned}$ | $\alpha_{x y}, \alpha_{x z}, \alpha_{y z}$ | - |
| - | - | $\mu_{x}, \mu_{s}, \mu_{z}$ | - |
| $\nu_{1}$ (symmetric muda) $V_{2}$ |  | $\nu_{s}$ (strechiny mode) $\nu_{H}$ (bending mode) |  |

where the transformation properties of the components of the polarizability and of the dipole moment are given.

In $\mathrm{CH}_{4}$ and $\mathrm{CD}_{4}$ a transition from ground level to level with $Q_{I}$ si ngly excited yields: $A_{I} \times\left(T_{2}\right)_{\mu} \times A_{I}=\left(T_{2}\right)_{\mu}$ which is not IR active as not containing the $A_{I}$, but it is Raman active ( $A_{I} \times\left(A_{I}\right) \times A_{I}=\left(A_{I}\right)$ ).

By similar calculations transjtions from ground level to levels of the type $\left(Q_{2}, Q_{3}\right)$ are not expected to be IR active, while transitions to $\left(Q_{4}, Q_{5}, Q_{6}\right)$ and ( $\left.Q_{7}, Q_{8}, Q_{9}\right)$ will be IR active. Likemise it can be shown that all transitions from the ground state are expected to be Raman active.

Anderson and Savoie ${ }^{(6)}$ measured the frequencies of the transitions for $\mathrm{CH}_{4}$ and $\mathrm{CD}_{4}$ molecules in the crystal which are tabulated in Tables I, II of the papere ${ }^{(6)}$ The results are in complete agreement with the predictions based on group theory.

The fact, as well as the absence of IR spectral activity in the $V_{i}$ and $V_{2}$ regions, suggest that the symmetry of $\mathrm{CH}_{4}$ and $\mathrm{CD}_{4}$ molecules in the cry
stal is substantially tetrahedral. As has been seen,the vibrational spectr um of the free molecule in the gaseous state depends essentially on the sya metry properties of the free molecule. In the condensed state, that is in the crystal,similar but not identical criteria apply.

The arrangement of the molecules in the crystal lattice is given by certain "space symmetry groups" together with the knowledge of how many mole cules occur in the unit cell, characteristics determining the nature of the vibrational spectra of crystals;such a table is given by Savitsky and Horn ig ${ }^{(15)}$ for methane (table II), based on the X-ray studies on crystalline methane done by A.Shallamach. (2) These show the carbon lattice to be essontially face centered cubic above and below the critical point $20.4^{\circ} \mathrm{K}$.

The necessity now to choose out of the possible space groups for the structure of phase II the ones which put the carbon atoms on face centered positions (allowing three infrared active components for $V_{4}$ ), led Savitsky and Hornig to hexagonal and tetragonal structures with two or four molecules per unit cell in which the carbon atoms lie on sites whose symetries are subgroups of $\mathrm{T}_{\mathrm{d}}$ and fit both their infrared data and the packing requiremen $t s ;$ but is found that groups $D_{2 d}^{2}$ and $D_{2 d}^{3}$ (from tableII) with two molecules per unit cell on sites of $D_{2}$ and $C_{2 v}$ symmetry respectivelly, are most favor -able.

However, the group $C_{2 v}$ is rejected since it predicts infrared activi ty for $V_{I}$ and $V_{2}$ and these were not observed even in very thin films. (e)

Hence the space groups $D_{2 d}^{2}$ and $D_{2}^{3}{ }_{2}^{3}$ represent the best packing and therefore the crystal in phase II has most probably this structure.

In addition it is also consistent with the Raman results oi Ander(6)
son and Savoie.
For the problem of phase I, the fact that the position of the peaks
does not changes as Savitsky and Hornig have noticed, on warmisg, but the bands broaden sigaificantly (width at $32^{\circ} \mathrm{K}$ of $\mathrm{CH}_{4}$ is 9 . Icm ${ }^{-1}$ while at $22^{\circ}$ is only $5 \mathrm{~cm}^{-I}$ ) supports the evidence for disorder: since the structure is disordered it cannot characterized by a space group (except in an average sense) as phase II。

In phase III we motice that more peaks exist in the absorption spec tra, which neans we bave further splitting of some lines and consequently a space group of lower symetry, but this is not exactly the case.

On the one hand $V_{3}$ is not further split, while $V_{4}$ its the $I R$ spectrvan is spilt into severi components.

Loweriak the symetry from $T_{d}$ to $D_{2 d}$ splits the triply degenerato $V_{4}$ mode into a singly degenerate (type $\mathrm{B}_{2}$ ) and a doubly degenerate (type E)moo de. Furthermore if the symetry changes to $D_{2}$ this mode splits into three simgly degemerate modes (types $\mathrm{B}_{\mathrm{I}}, \mathrm{B}_{2}, \mathrm{~B}_{3}$ ) o

In either case table $I I^{(15)}$ shows that there are 2 molecules per unit cell, so that the marimun number of lines that can occur, taking into account the Davydov splittingis 4 or 6 respectively. So a possible explanatioa is to require more molecules per primitive cell, but in anyway the situation regardiag phase III is uncleargsince $i$ it is not even known whether the face centered structure is retained in this phase.
(I): K.Clusius, Z.Physic.cher(LeipziE) B3. 4 I(I929)
(2): RoShallamach, Proc.Roy.Soc(London) AI7Is 569(I939)
(3): SoGreer, Lereyex, JoChemoPlys. 52: 468(I970)
(4): HoJanes, To Keenan, JoCher, Phys, 3Is I2(I959)
(5): To Tagamiya, Froge Theor. Phys. (Kyoto) 6, 702(I95I)
(6): AoAndexson. Rosavoie, J. CherePhys 43. 3468 (I965)
(7): W.Press $\mathrm{J}_{0}$ Chera Phys 56, 2597(1972)
 bille.1955) , pages II7-125
(9): H.Janes, J.Raich, Phys.Rev I62, 649(I967)
(IO): $P_{0}$ Dumare ${ }_{8} J_{0}$ Chemophys (to be published)
(II): T. Yamanoto, XoKataoka, J.Chemo.Phys 48. 3I99(I968)
(I2): D.Goodings Persomal notes
(I3): Joketelaax SpecrochimoActa I5 $^{2}$ 237(I959)

AoChamberland: Robeizile AoCabasas. Can out Chen 48, II29(I970)
(I5): GoSavitsky ${ }_{8}$ DHormigg $_{g} J_{0}$ Chem. Phys 36, 2634(I962)

